

**Rough English translation**

**DE4406431 C2 1996-06-05 Procedure for the production more porously, more gaspermeabler, catalytically effective parts with internal surfaces (en)**

**Verfahren zur Herstellung poröser, gaspermeabler, katalytisch wirksamer Teile mit inneren Oberflächen (de) - Abstract**

**English Abstract:**

Procedure for the production more porously, more gaspermeabler, catalytically effective parts (10) with internal surfaces (15) for the catalysis of chemical reactions of or with gases (11) or as getter (13) by mixing powders the substrate of forming part (of 10) marked by form-coining/shaping, if necessary metals of group of platinum on their surface as catalytically effective means (13, 14) exhibiting powders as well as following sinters of the mixture under removing the form-coining/shaping means (12), thereby that as form-coining/shaping means (of 12) powders from Picein, Thermalruß, Theobromin, Indigo, polyethylene or mixtures of these materials and as catalytically effective means RH, Pd and/or Pt and/or getter materials from alkaline-earth oxides or mixed, made of the metals ME I and ME III existing oxides of the formula ME I ME III CO<sub>2</sub>, in particular LiAlO<sub>2</sub>, to be used and that the catalytically effective means (13, 14) after the burning out out and/or evaporation of the form-coining/shaping means (12) in the pores of the part (10) verbleiben.SA

**▼ Bibliographic Data**

**Applicants/Assignees:** Robert Bosch GmbH, 70469 Stuttgart, DE

**Inventors:** Friese, Karl-Hermann, Dipl.-Phys. Dr., 71229 Leonberg, DE ;

Weber, Lothar, Dr., 70499 Stuttgart, DE ;

Gruenwald, Werner, Dipl.-Phys. Dr., 70839 Gerlingen, DE

**Application Number:** DE4406431 A

**Application/Filing Date:** 1994-02-28

**Classifications:** ECLA: B01J35/02; B01J37/08 IPC[6]-Main: B01J 37/08 A, IPC-1-8:

B01J35/00 20060101C I20051008RMEP (20060101) Core20051008 (C I R M EP)

IPC-ADDL-CL: B01J35/02 20060101A I20051008RMEP (20060101)

Advanced20051008 (A I R M EP)

IPC-ADDL-CL: B01J37/00 20060101C I20051008RMEP (20060101) Core20051008 (C I R M EP)

IPC-ADDL-CL: B01J37/08 20060101A I20051008RMEP (20060101)

Advanced20051008 (A I R M EP)

**▼Patent References Cited-Forward:**

**Retrieve Selected**

Publication Number	Publication Date	Title	Applicant/Assignee
DE19906306C2	2003-12-18	Verfahren zur Herstellung von Cermetelektroden für Meßfühler	Robert Bosch GmbH, 70469 Stuttgart, DE

▼ **Description**

**English Description:**

The invention concerns a procedure for the production more porously, more gaspermeabler, catalytically effective parts in accordance with the kind of the principal claim.

From the GB-PS 11 10 852 a such procedure for the production of a catalyst is well-known, with which a powdered substrate is mixed with a powdered filler, the one active substance, for example a metal of group of platinum, on its surface exhibits. This mixture is sintered afterwards under complete distance of the wadding.

During sintering of mixtures of catalytically active materials with ceramic(s) powders the catalytically active means are fully enclosed mostly by ceramic(s), whereby a high materials consumption becomes necessary for the acquisition of sufficient catalytic activity. For bringing catalytically active materials into porous ceramic parts by impregnation with a salt solution ceramic(s) with means, which coin/shape the cavity form and which attitude to porosity permit, is sintered, impregnated and again heated up. An even distribution of the catalytically active means after thermal distance of the form-forming means on the internal surface of the ceramic, permeable part is not always reached thereby satisfying. The usable surface on the inside of the ceramic part lies catalytically ineffectively fallow.

Task of the invention is it to train a procedure further of the kind initially specified dahingend that permeable parts distributed figuration regret, porous, on surfaces on the inside with even over this internal surface catalytically active means and/or getter materials be coated can; the procedure is itself for automatable production of parts is suitable.

This task is solved by procedures according to invention indicated in the patent claim. A form screen end a means, which is a thermally decomposable, burn outable and/or evaporatable material, makes possible here, to apply on the internal surfaces of the part catalytically active materials. The range of the catalytically active means in the part, thus specified, increases its effective surface for the purpose of the catalysis.

Because of the higher catalytically effective surface the materials consumption of the catalytically active means and the form-coining/shaping means can be reduced with same catalytic effectiveness. A reduction of the catalytically effective part is possible and the mass decrease of the part extends the mobile employment. By the better uniform

distribution of the catalytically active material a clear improvement of the life span of the part enters. With large form-coining/shaping means it is possible to cover coherent internal surface ranges of the part with catalytically active material. Regarding the production of the part the procedure is needed simplified, as no impregnation is more necessary for bringing in the catalytically active means, the one thermal subsequent treatment.

If two or more different catalytically active means are used, then it is possible to develop under utilization of the architecture of a form-coining/shaping means with the catalytically active means a catalyst at the internal surfaces of the part with that the catalytically active means in a firm spatial relationship to each other. In addition different density gradients of mixtures of the catalytic active means are adjustable. It is no more problem to manufacture a catalyst on the internal surfaces of the part, composed of several layers.

By applying the catalytically effective means on the surface of the form-coining/shaping means connected ranges or samples can be provided with catalytically active material on the internal surfaces of the part.

By different catalytically effective means on the surface of the form-coining/shaping means it is possible to adapt the catalytically effective parts different chemical reaction conditions. Around for example CO, HC, to convert NO<sub>x</sub> and O<sub>2</sub> in automobile exhaust gases into the thermodynamic equilibrium are preferably RH-catalysts with deep, Pt-catalysts at high temperatures next to each other effectively. By the coating according to invention a separation of catalytic means is possible, which would mix otherwise and by it their effect to lose. An alloy formation of Pt with RH can be avoided in such a way.

In particular if the powder grains exhibit approximately spherical shape, a particularly favorable relationship of surface volume becomes usable with firm pore radius for the catalysis. Furthermore the permeability of the part with well-known dimensions can be stopped purposefully by the choice of the dimensions of form-coining/shaping means and with catalytically active means provided form-coining/shaping means.

With the procedure according to invention it is possible to bind the catalytically active means in a simple manner to the form-coining/shaping means.

An additive from Theobromin to thick-film pastes and/or ceramic molding materials, the basic substance of the part, which sublimates during sintering and defined cavities leaves, is suitable excellently for the automated simmering jerk technology.

The figure shows a cut by a porous part with catalytically effective coatings on the pore surfaces.

In detail it shows schematically a porous part **10**, which is manufactured in the procedure according to invention. The channel **16** grew together from closed-up pores **12**, whose internal surfaces exhibit **15** catalytically active means **13** and/or **14**. Furthermore is

insulating, for example spherical, catalytically ineffective pore 17 in the part 10 represented. The porous part of 10 is from zirconium dioxide ceramic(s), the catalytically active means 13 is a getter or a getter from oxides, preferably alkaline earth metal oxides, and the catalytically active means 14 is a precious metal, in particular platinum or a rhodium. A gas 11, for example the exhaust gas of a thermal engine, flows from the surface of the permeable part of 10 into the channel 16 to the back of the part of 10 and withdraws there. Isolate lying pores are isolated recognizably.

The form-coining/shaping means will become by chemical Fällprozesse, by dead separating on Pulverteilchen, by vaporizing Pulverteilchen, by laser-induced decomposition of gases on Pulverteilchen or in the fluid bed coated with types of dust on the Pulverteilchen with catalytically active means 13, 14 or these catalytically active means brought into the volume of the form-coining/shaping means. The subsequent treatment of a catalytically effective platinum layer for the increase of the adhesive strength on Picein took place favourably in the nitrogen-hydrogen mixture stream with 900 degrees Celsius, for rhodium as catalytically active means is 1000 degrees Celsius more favourably. As nitrogen-hydrogen mixture a mixture of 10 parts hydrogen and 90 parts nitrogen was used.

For the production of the part of 10 powders, which form the material of the part of 10, with powders of form-coining/shaping means, which unite catalytically active means 13, 14 to exhibit, are mixed, agitated or sprayed preferably and sintered afterwards. The Sintertemperatur of the mixture lies between 500 and 1600 degrees Celsius for zirconium dioxide powders with Piceinpulver of a firm grain size of 4 micrometers diameters. The contraction of the part of 10 leads to a diameter of the pores, which is smaller than the original grain diameters of the form-coining/shaping means with catalytically active means. As form-coining/shaping means with platinum recompensed Picein, with rhodium recompensed Theobromin or with larger form-coining/shaping grains platinum beside rhodium are preferably used. There is also grains with partial coating one or several catalytically active means secondary or one on the other applicable. The different particle size and - form is visible in the figure. Also getter substances, for example  $\text{LiAlO}_2$ , can be used in place of catalytically active substances.

#### Comparison example

For the production of a porous ceramic(s) part a Thermalrußpulver with a grain size of 1 to 150 micrometers grain diameter with a zirconium dioxide powder, which contains weight percentage Yttriumoxid up to 5, with an organic binder and with a softener under additive of a solvent will grind 10. After sintering with 1600 degrees Celsius one receives a porous ceramic(s) part. Alternatively Indigo, Picein, polyethylene wax or Theobromin as form-coining/shaping means are used.

#### Example 1

For the production of a porous ceramic(s) part 10 with catalytically effective substances a powder, as in the comparison example described, is used, after it was coated preceding

with platinum. The form-coining/shaping means is recompensed at its surface by chemical Fällprozesse, in particular reduction of metallic salt solutions, which lead to the separation of catalytically wirsamem platinum or rhodium.

#### Example 2

A powder substance from Theobrominpulver with platinum layer and zirconium dioxide powder is over-laminated and sintered by a powder substance from Piceinpulver with rhodium layer and zirconium dioxide powder.

#### Example 3

For the production of a rectangular channel of 100 micrometers channel height 165 micrometers thick and 165 micrometers a broad layer from paste on a ceramic carrier is printed, whereby by the more largely selected measures the contraction was considered. The paste was descriptive manufactured as in the comparison example in example 1, however no zirconium dioxide and Yttriumoxid were used. The received pasty mass is imprinted by means of a usual automated silk-screen printing on a ceramic carrier. In addition also the so-called "Tampenprint" - procedure can be used. After applying a ceramic resist coating this resist coating in the nitrogen stream is strengthened with 900 degrees Celsius. In a following fuel step at air or in oxidizing atmosphere the form-coining/shaping means are arrears-free burned out. Sintering follows with 1600 degrees Celsius.

For the examples specified above it proved favourably as for the Porengröße at the most the 0,2fachen value of the layer thickness of the ceramic(s) part which can be manufactured to select itself, which corresponded to a range of application of 2 to 15 micrometers. The layer thickness of the applied catalytically effective material on the Formpräger was particularly favourable, if the diameter of the form-coining/shaping grains constituted the tenfold value of the layer thickness of a schichtförmigen catalytically effective substance. By the grain size of the form-coining/shaping means before definable by means of seven the porosity of the part of 10 becomes definable regarding partial density, permeability and the diameter of the pores. As form-coining/shaping means for ceramic(s) parts are usable dust, suspensions, pastes, granulates, fixed particles or prefabricated volume parts for ceramic(s) partial production.

#### **Claims**

**Number of Claims: 2**

#### **ENGLISH CLAIMS:**

Procedure for the production more porously, more gaspermeabler, catalytically effective parts (10) with internal surfaces (15) for the catalysis of chemical reactions of or with gases (11) or as getter (13) by mixing powders the substrate of forming part (of 10) with form-coining/shaping, if necessary metals of group of platinum on their surface

gekennzeichnet als katalytisch wirksame Mittel (13, 14) aus Pulvern sowie als  
folgende Sinterungen der Mischung unter Entfernung der Formschneid-/Formgebungs-  
mittel (12), wobei das als Formschneid-/Formgebungs- (12) Pulver aus Picein, Thermalruß,  
Theobromin, Indigo, Polyethylen oder Mischungen dieser Materialien und als katalytisch  
wirksame Mittel RH, Pd und/oder Pt und/oder Gettermaterialien aus alkalischen-Erden-  
oxiden oder Mischungen, bestehend aus den Metallen Me1 und My sowie Oxiden der  
Formel  $Me1Me2O_2$ , insbesondere  $LiAlO_2$ , verwendet werden und dass die katalytisch wirksamen Mittel (13,

14) nach dem Ausbrennen und/oder Verdampfen der Formschneid-/Formgebungs-  
mittel (12) in den Poren des Teils (10) verbleiben. Für diese 1. Ausführungsform ist die  
Herstellung eines rechteckigen Kanals mit einer Kanalhöhe von 100 µm und einer  
Kanalwandstärke von 165 µm auf einem Keramikträger beschrieben, wobei die  
Kanalwandstärke von 165 µm eine Schicht aus Pulver darstellt, die auf dem Träger  
aufgebracht wurde, wobei die Schicht als Schicht aus Pulver auf dem Träger  
betrachtet werden kann, wobei die Schicht als Schicht aus Pulver auf dem Träger  
betrachtet werden kann. Die Schicht wurde als Schicht aus Pulver auf dem Träger  
hergestellt, wie in dem Vergleichsbeispiel in Beispiel 1, jedoch ohne Zirkon